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Procedure for the Mathematical Determination of Total Heat of Combustion Content of Solid Wastes

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The heat contents of various solid wastes materials (usually expressed as: British Thermal Units per pound or Btu/# of sample) are important to establish an energy balance about an incinerator and thereby determine the efficiency of that incinerator. Also this heat value, especially of raw refuse, is considered when planning the design of an incinerator. The heat contents of incinerator residue and compost used for landfill are essential data for determining the stability of these waste products.

The experimental method 1, 2 of determining heat contents of prepared solid waste samples 3 is sometimes difficult to perform and the accuracy of the data is, at times, questionable. The heat contents of such samples may be determined mathematically by a modified Dulong formula 4 with data from ultimate analysis. This mathematical approach can either eliminate the need for experimental test or verify the accuracy of such test. Total heat of combustion content of a solid waste sample is defined as the oxidation of organic carbon to carbon dioxide, hydrogen to water, nitrogen to nitrogen dioxide, sulfur to sulfur dioxide, and the decomposition of carbonates present in the sample.

17a. Descriptors

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*Heat of combustion,
*Chemical analysis,
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PROCEDURE FOR THE MATHEMATICAL DETERMINATION OF TOTAL HEAT OF COMBUSTION CONTENT OF SOLID WASTES

A Solid Waste Research
Open-File Report (RS-03-68-17)

written by
DONALD L. WILSON, Research Chemist

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Monitoring
Solid Waste Research
1971

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DISCUSSION

The heat contents of various solid wastes materials (usually expressed as: British Thermal Units per pound or Btu/# of sample) are important to establish an energy balance about an incinerator and thereby determine the efficiency of that incinerator. Also this heat value,especially of raw refuse, is considered when planning the design of an incinerator. The heat contents of incinerator residue and compost used for landfill are essential data for determining the stability of these waste products.

The experimental method[1],[2] of determining heat contents of prepared solid waste samples[3] is sometimes difficult to perform and the accuracy of the data is, at times,questionable. The heat contents of such samples may be determined mathematically by a modified Dulong formula[4] with data from ultimate analysis. This mathematical approach can either eliminate the need for experimental test or verify the accuracy of such test.

The formula for calculating Btu/# content in solid wastes samples correlates data from fourteen different analyses. The six directly employed components are: (1) organic carbon[5],[6], (2) total hydrogen[5], (3) organic oxygen[6],[7],(4) total nitrogen[8], (5) total sulfur[2],[9], and (6) carbonate carbon[6]. The eight related analyses are: (1) total carbon[5], (2) carbonate carbon in ash for volatile at 600 C[6],[7], (3) decomposition of carbonates at 600 C[6],[7], (4) volatile at 600 C value[7],[10], (5) volatile at 950 C value[7],[11], (6) total oxygen[7], (7) carbonate oxygen[6],[7], and (8) total chlorine[7],[12]. The heat of combustion method, described herein, deals with the procedures for the six directly related components.

The modified Dulong formula still has the errors inherent in the other analysis; however, the agreement between experimental and mathematical Btu/# values is about equal to the agreement between replicate experimental Btu/# values[4].

Total heat of combustion content of a solid waste sample is defined as the oxidation of organic carbon to carbon dioxide, hydrogen to water, nitrogen to nitrogen dioxide, sulfur to sulfur dioxide, and the decomposition of carbonates present in the sample.

APPARATUS

This procedure requires no apparatus other than what is needed for the fourteen different analyses that must be performed to obtain the data for thismethod.

REAGENTS

No reagents are necessary for this analysis. Reagents are needed for the fourteen correlated methods and are mentioned in the appropriate method.

SAFETY PRECAUTIONS

No safety hazards exist in this procedure. Safety precautions necessary in related methods have been discussed in those methods.

SAMPLE PREPARATION

Preparation of solid wastes samples are discussed in the carbon-hydrogen method[5] and elsewhere[3]. Therefore, sample preparation techniques are not repeated in this method.

PROCEDURE

Carbon-Hydrogen Analyses

Procedure	Comments
1. Determine total carbon and hydrogen contents of solid wastes samples by the method developed particularly for solid wastes samples. (See reference #5)	1. a) With this method larger sample portions are analyzed than with similar methods. b) The total carbon value will be used in conjunciton with the carbonate carbon value to determine the organically-bonded carbon content.
NOTE: At the same time, loss-on-ignition @ 950 C may be determined. (See references #7 and #11).	

Oxygen Analysis

Procedure	Comments
1. Determine total content of solid wastes samples by the method developed particularly for solid wastes samples. (See reference #7)	1. a) This method overcomes difficulties when appling an ASTM oxygen method to solid waste samples. b) The organically-bonded oxygen content of the sample is determined from the total oxygen content and the carbonate oxygen content. The carbonate oxygen content is calculated from the carbonate carbon content.
NOTE: Chlorine content is determined during this analysis. (See references #7 and #12)	

Nitrogen Analysis

Procedure	Comments
1. Nitrogen content of solid samples is determined by one of the recommended methods for solid waste. (See reference #8).	1. The Kjeldahl-Wilfarth-Gunning-Winkler Method is the one that is most commonly used for solid waste samples. However, this method does not include nitrate nitrogen in the total nitrogen data.
2. Nitrogen content of incinerator raw refuse, incinerator combustible residue, and compost samples may be estimated to be 0.75%.	2. This estimate is the average nitrogen content of twelve raw refuse samples. These nitrogen contents ranged from 0.49% to 1.42%.
3. Nitrogen content of incinerator non-combustible-residue samples and incinerator fly ash samples may be estimated to be 0.15%.	3. This estimate is the average nitrogen content of nine non-combustible-residue samples. The nitrogen concentrations ranged from 0.04% to 0.31%.

Sulfur Analysis

Procedure	Comments
1. Sulfur content of solid wastes samples may be determined by an ASTM method. (See reference #2 and #9).	1. a) This method is the one most commonly used for solid wastes samples. (See reference #9).

b) The related bomb-combustion method was developed especially for solid wastes samples. (See reference #2).

2. Sulfur content of solid wastes samples (raw refuse, incinerator residue, incinerator fly ash, and compost) may be estimated to be 0.20%.

2. The exact average sulfur content of twenty-one samples (twelve raw refuse and nine non-combustible-residue samples) was 0.19%. The sulfur concentration ranged from 0.10% to 0.37%.

Carbonate Carbon Analysis

Procedure

1. Determine carbonate carbon content of solid wastes samples by the method developed particularly for solid wastes samples. (See reference #6).

Comments

1. This analysis is also needed to distinguish organic carbon from total carbon and organic oxygen from total oxygen.

STANDARDIZATION AND CALIBRATION

No standardization and calibration are required for this procedure. These techniques are disclosed in the methods associated with this analysis.

CALCULATIONS

1. Formula for total heat or combustion content (Btu/#) of solid wastes:

$$\text{Btu/\#} = 14{,}096\ C_o + 60{,}214\ (H - \tfrac{O}{8}) + 1040\ N + 3982\ S$$

$$+8929\ \frac{(H - \frac{O}{8})}{2} + 4274\ (\tfrac{O}{2}) - 6382\ C_i$$

Where: Btu = British thermal units

= a pound of sample

14,096 = the heat of combustion, in Btu/#, of graphite carbon

C_o = the decimal percent of organically-bonded elemental carbon

60,214 = the heat of formation, in Btu/#, of liquid water (constant volume) from hydrogen and oxygen gases

H = the total decimal percent of the element hydrogen

O = the decimal percent of organically-bonded oxygen

$(H-\frac{O}{8})$ = the decimal percent of available hydrogen

N = the total decimal percent of the element nitrogen

S = the total decimal percent of the element sulfur

C_i = the decimal percent of inorganically-bonded (carbonate) elemental carbon

NOTE: a) N and S may be estimated if not actually determined.

b) All results are on a dry basis (prepared samples).

2. Formula for total % organically-bonded carbon:

$$\% C_O = \%C - \% C_i$$

Where: % = the decimal percent by weight

C = the element carbon (total)

3. Formula for % carbonate oxygen:

$$\%O_c = (\frac{4}{1})(C_i)$$

Where: % = the percent by weight

O_c = inorganically bonded (carbonate) elemental oxygen

4. Formula for % organically-bonded oxygen:

$$\%O \text{ or } \%O_o = \%O_t - \%O_c$$

Where: % = the percent by weight

O or O_o = organically-bonded elemental oxygen

O_t = the element oxygen (total)

5. Conversion of data from a wet basis to a dry basis:

$$\% X_d = (100)(\%X_w) \div (100-m)$$

Where: % = the percent by weight

X_d = the ingredient on a dry basis, except volatiles

X_w = the ingredient on a wet basis, except volatiles

m = the percent of moisture (loss-at-105 C)

Volatiles only:

$$\%V_d = (V_w-m) \div (100-m)$$

Where: % = the percent by weight

V_d = the volatile portion of the sample, dry basis

V_w = the percent volatile portion of the sample, wet basis

METHOD EVALUATION

The accuracy of this method is dependent upon the accuracy of the related analyses and the care shown in removing glass, ceramics, and metals during sample preparation.

When this procedure was applied to sixty-one samples from five incinerators[4] the data revealed that the variation between calculated Btu/# values and experimental Btu/# values has about the same magnitude as the variation between replicate experimental values. These calculated Btu/# values are well within limits of requirements for an estimated Btu/# value of solid waste samples.

Th time required to perform the calculations for the Btu/# value is short, but the related laboratory analyses required are very time consuming; however, such analyses are generally not performed for just a Btu/# value. The same ultimate analysis data is used for establishing a material balance about the same incinerator and thereby determine also the efficiency of that incinerator to reduce the volume of solid wastes material.

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